

### REMARKS

Claim 8 has been amended to better define the present invention.

Claims 8-14 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Downey (U.S. Patent 5,762,891) in view of Krause (U.S. Patent 5,820,966). The present invention is directed to a method of selectively precipitating arsenic from a solution containing copper, ferric iron and ferrous iron whilst minimizing copper losses through co-precipitation by using a two-step process of calcium-containing neutralizing agent addition. Applicant submits that neither of the references cited teach or suggests a two-step process of calcium-containing neutralizing agent addition. Furthermore, Applicant submits that it would not be obvious to use the two-step process claimed by the Applicant. Downey teaches that a treated solution (subsequent to arsenic precipitation) may be subjected to treatment steps to recover dissolved metals such as copper (col. 8, lines 40-50). The Examiner relies on this disclosure to support an assumption that, because copper may be recovered from solution, the copper must have stayed in solution and therefore copper loss was minimized. Applicant submits that this assumption is made under the influence of hindsight for, clearly, copper can still be recovered from solution if copper losses are not minimized. The Downey reference is devoid of any quantification regarding copper concentration before and after arsenic precipitation. The disclosure cannot therefore support the contention that Downey teaches a method of selectively precipitating arsenic whilst minimizing copper losses. However, the Applicant can objectively show, from the attached paper on a laboratory study, conducted by P.I. Harvey (one of the listed inventors) in September 1999, that copper loss through co-precipitation is minimized when the method of the present invention is carried out. The study shows, at 85 °C (Figure 6) and 60 °C (Figure 7) respectively, using lime

as the neutralizing agent, that between pH 1.5 and pH 2.2, copper removal remains minimal whilst arsenic and iron removal is high. Figures 6 and 7 correspond with batch tests B6 and B7, respectively. The batch test results were used to conduct a series of continuous neutralization tests, which better emulate the practical environment. Continuous neutralization tests C4 and C5 were conducted using the same solutions as batch tests B6 and B7. The results of the continuous neutralization tests show (Tabel 7), at pH setpoints of 2.15 and 2.25, that:

- 1) for tests C4 (85 °C), only 1.54% of the copper is removed whilst 54.9% of the arsenic is removed; and
- 2) for test C5 (60 °C), only 0.43% of the copper is removed whilst 60.2% of the arsenic is removed.

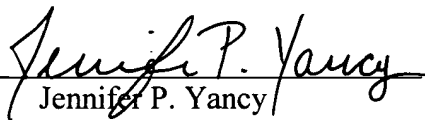
It is known that washing reduces copper co-precipitation. Therefore, it may be expected that more favourable results would occur had results been obtained after washing.

The results of tests C4 and C5 also support another advantage of the invention, i.e. the method is equally effective at temperatures as low as 60 °C. The advantage of this is that at temperatures just above 85 °C, in high altitude locations such as Chile, the boiling point of water is being reached. Numerous technical and economic difficulties are posed by the design of a plant capable of working at temperatures close to boiling point.

The advantage of using a two-step process of neutralizing agent addition is that it provides better pH control. By adding the neutralizing agent in a step-wise manner, localized areas of relatively high pH are avoided and thus copper co-precipitation in these high pH localities is reduced. Furthermore, better nucleation of the arsenate precipitate, and a better seed material, result from the step-wise addition of the neutralizing agent.

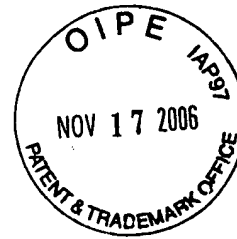
For the foregoing reasons, Applicant submits that the rejection has been overcome and requests reconsideration and allowance of the claims of the present application.

Respectfully submitted,

By:   
Jennifer P. Yancy  
Reg. Number 47,003

JONES, TULLAR & COOPER, P.C.  
P.O. Box 2266 Eads Station  
Arlington, VA 22202  
(703) 415-1500

Filed: 17 November 2006



**CONFIDENTIAL**

**REPORT NO PR 99/71**

**Project No 99/171**

**BioCOP® PRODUCT NEUTRALISATION**

**2 September, 1999**

**By**

**P I Harvey: Principal Research Metallurgist**

A handwritten signature in black ink, appearing to read 'D D Slatter'.

**Dr D D Slatter**  
**MANAGER**  
**Ar**

**Private Bag X10014**  
**RANDBURG**  
**2125**  
**South Africa**  
**Tel: (011) 792 7090**  
**Fax: (011) 792 7097**

**Client: Minerals Technology - BioCOP®**

**DISTRIBUTION**

Dr A K Haines	Chief Executive	BILLITON Minerals Technology
Mr P M Craven	Senior Consulting Metallurgist	BILLITON Minerals Technology
Mr R Way	Consulting Metallurgist	BILLITON Minerals Technology
Mr A Norton	Consulting Metallurgist	BILLITON Minerals Technology
Mr J D Batty	Process Manager	BILLITON Minerals Technology
Dr J M Schaekers	Manager : Process Chemistry	BILLITON Process Research
Dr D W Dew	Manager : Process Development	BILLITON Process Research
Mr P I Harvey	Principal Research Metallurgist	BILLITON Process Research
Mr G V Rorke	Principal Research Metallurgist	BILLITON Process Research

BILLITON S.A. Information Centre

This document is issued as a means of communication of information to the persons or companies concerned. It may not be passed on to any other person or company, must not be quoted as a reference or be included in a bibliography, nor may the contents be reproduced in part or in whole without written permission from BILLITON.

**TABLE OF CONTENTS**

	page
1. INTRODUCTION	1
2. OBJECTIVES	1
3. NEUTRALISATION TEST SOLUTIONS	2
4. SCORODITE SEED FORMATION	2
5. pH OF INDUCTION TESTS	3
6. BENCH SCALE NEUTRALISATION TESTS	4
6.1 Experimental Procedure	4
6.2 Results and Discussion	5
7. NEUTRALISATION POSITIONS WITHIN THE BIOCOP® PROCESS	8
7.1 PLS Feed Solution	8
7.2 Bioleach Decant Thickener Overflow Solution	9
7.3 Raffinate Bleed Solution Produced by the SX / EW Circuit	10
7.4 Bioleach CCD Wash Water	11
7.5 Conclusions	12
8. PILOT PLANT NEUTRALISATION TESTS	12
8.1 Pilot Plant Description and Experimental Procedure	13
8.2 Results and Discussion	15
9. LIQUID-SOLID SEPARATION TESTS	18
9.1 Polymer Selection	18
9.2 Bulk Sedimentation Tests	18
9.3 Neutralised Product Thickening Test	18
9.4 Filtration Tests	19
9.5 Recommendations	19
10. CONCLUSIONS	20
11. RECOMMENDATIONS	20
12. REFERENCES	21
APPENDIX 1 : BATCH TEST RESULTS	22
APPENDIX 2 : CONTINUOUS TEST RESULTS	28

## 1. INTRODUCTION

One of the major advantages of the BioCOP<sup>®</sup> process is that it allows ores containing arsenic minerals to be processed with no adverse environmental impact. This is achieved by neutralisation of solution streams containing solubilised arsenic. The process streams in the BioCOP<sup>®</sup> process that contain solubilised arsenic also contain leached copper. Conventional neutralisation will precipitate all the copper out of the solution due to the high pH used. Thus the BioCOP<sup>®</sup> neutralisation process will differ from that currently used in BIOX<sup>®</sup> plants. It is necessary, therefore, to identify a neutralisation process that will remove arsenic and iron from solution without significant co-precipitation of copper.

The exact position of the neutralisation step within the BioCOP<sup>®</sup> flowsheet is yet to be established. Ideally the process should be positioned to treat the PLS stream prior to SX. At this stage in the process, precipitation of iron from solution will lower the ferric concentration entering the SX plant, thereby reducing degradation of the organic phase and extraction of iron. Neutralisation at this stage, however, may result in significant copper losses due to the high copper tenor of the solution. Neutralisation may also be performed on the bioleach decant thickener overflow solution, the CCD wash water solution and on a bleed raffinate stream. At these stages in the process, copper co-precipitation should be less significant due to the lower copper content of the respective streams. The advantages and disadvantages of each neutralisation position in the BioCOP<sup>®</sup> flowsheet are discussed in this report.

A process pioneered by Hatch / Hydro-Terra was identified as the technology most likely to promote precipitation of iron and arsenic without significant copper losses. The process utilises controlled supersaturation of the solution, allowing crystalline scorodite and jarosite to be precipitated. The crystalline nature of the precipitate minimises copper co-precipitation, and increases the settling rate and filtration characteristics of the precipitate.

A number of alternative processes were tested previously at BILLITON Process Research, both on bench and pilot plant scale. In addition to the Hatch / Hydro-Terra process, conventional neutralisation and neutralisation at low pH to form amorphous ferric arsenate and jarosite was tested. The crystalline scorodite process did not yield promising results, as the production of scorodite for the testwork was not successful. Amorphous ferric arsenate precipitation at 60°C resulted in relatively little copper loss together with an acceptable product settling rate. The product was stable and the process control easier than at higher temperature<sup>(1)</sup>.

This report details the bench and pilot plant scale neutralisation testwork repeated on synthetic solutions and on solutions produced by the Smarties pilot plant in Chile. Liquid-solid separation testwork was conducted on neutralised product.

## 2. OBJECTIVES

The objectives of the neutralisation testwork are as follows:

1. Determine the applicability of the Hatch / Hydro-Terra process and amorphous ferric arsenate precipitation of BioCOP<sup>®</sup> product streams produced by the pilot plant in Chile
2. Establish the extent of copper co-precipitation at the alternate neutralisation positions within the BioCOP<sup>®</sup> process
3. Identify the most suitable position of the neutralisation process in the BioCOP<sup>®</sup> flowsheet
4. Verify the environmental stability of the precipitate formed by the standard Toxicity Characteristic Leaching Procedure (TCLP)
5. Establish the settling and filtration characteristics of the neutralisation product

### 3. NEUTRALISATION TEST SOLUTIONS

A summary of the feed characteristics of the solutions used for the neutralisation tests is shown in Table 1.

Table 1: Feed Characteristics of Test Solutions

Test	Fe(T) (g/L)	Fe(3+) (g/L)	Fe(2+) (g/L)	As(5+) (g/L)	Cu(T) (g/L)
pH of Induction Tests					
P1	1.50	1.50	0.00	1.03	29.0
P2	1.50	1.50	0.00	0.95	29.0
P3	1.60	1.60	0.00	0.98	18.0
P4	1.60	1.60	0.00	1.04	18.0
P5	2.30	2.30	0.00	1.05	18.0
P6	2.30	2.30	0.00	1.10	28.5
P7	2.30	2.30	0.00	1.10	28.5
P8	4.70	4.70	0.00	1.89	18.5
P9	7.42	7.42	0.00	1.59	6.10
P10	7.11	3.28	3.83	0.50	13.0
P11	9.39	2.59	6.80	0.50	13.0
Batch Neutralisation Tests					
B1	4.06	4.06	0.00	1.82	25.2
B2	4.28	4.28	0.00	1.92	26.2
B3	8.06	2.70	5.36	0.40	11.7
B4	8.21	2.70	5.51	0.40	11.7
B5	7.23	7.23	0.00	1.60	5.95
B6	15.6	7.59	8.01	0.79	26.8
B7	15.6	7.59	8.01	0.79	26.8
B8	17.8	17.3	0.50	3.20	20.2
B9	17.8	17.3	0.50	3.20	20.2
Continuous Pilot Plant Tests					
C1	6.51	6.51	0.00	1.01	13.9
C2	9.11	2.69	6.42	0.45	11.7
C3	7.90	7.90	0.00	1.72	5.99
C4	15.7	6.40	9.30	0.78	27.6
C5	16.0	6.40	9.60	0.79	27.6
C6	21.9	21.1	0.80	3.05	20.3
C7	21.9	21.1	0.80	3.05	20.3
C8	21.9	21.1	0.80	3.05	20.3

The pH of Induction tests (P1 – P13), batch tests (B1 – B5) and continuous tests (C1 – C3) were conducted on synthetic solutions. Batch tests (B6 – B7) and continuous tests (C4 – C5) were conducted on PLS solution produced by the Smarties pilot plant in Chile. Batch tests (B8 – B9) and continuous tests (C6 – C8) were conducted on bioleach decant thickener overflow solution produced by the Smarties pilot plant in Chile.

### 4. SCORODITE SEED FORMATION

Bryn Harris of Hatch Montreal produced scorodite crystals at McGill University by using high temperatures and pressures in an autoclave. The crystals were to be used for seeding of the bioleach solutions. Scorodite seed crystals were reported by D Droppert to be necessary to prevent precipitate scaling on the equipment, and to provide a site for the slow growth of well-formed scorodite crystals<sup>(2)</sup>.



It was subsequently found that when the PLS solution, produced by the pilot plant in Chile, was heated to 85°C, amorphous precipitate was formed which coated the scorodite crystals. This eliminated the possible positive aspects of using scorodite crystals for seeding and crystalline growth during neutralisation of PLS solution. The seeding concentration recommended by D Droppert is between 30 g/L and 50 g/L<sup>(3)</sup>. This implies that between 780 grams and 1300 grams of scorodite seed would be required to seed the four neutralisation reactors per continuous neutralisation test. Due to the cost of the scorodite seeds, (R16 666 for 2 kg), no further seeding testwork was conducted on the PLS solution produced by the pilot plant in Chile.

Further batch scorodite seed testwork will be conducted on bioleach decant thickener overflow solution produced by the pilot plant in Chile. The bioleach decant thickener overflow solution does not form an amorphous precipitate when heated to 85°C and hence scorodite seed testwork may be beneficial.

##### 5. pH OF INDUCTION TESTS

The pH of induction ( $pH_{ind}$ ) is the pH at which precipitates change in nature from crystalline to amorphous. The  $pH_{ind}$  varies greatly with differing solution compositions. In practice any changes in solution composition would have to be accompanied by a change in the pH set-point for the neutralisation process. It is necessary to identify this pH to determine the pH at which the continuous process is to operate to produce a crystalline precipitate.

The  $pH_{ind}$  testwork was carried out by heating and agitating a volume of each synthetic neutralisation solution to 90°C. Magnesium hydroxide slurry was added slowly to the test solutions. The  $pH_{ind}$  was then determined visually as the point at which the precipitate formed does not re-dissolve. Magnesium hydroxide slurry was used instead of lime or limestone to prevent the formation of gypsum, which could obscure the endpoint. A summary of the  $pH_{ind}$  testwork results conducted on synthetic neutralisation solutions is shown in Table 2.

Table 2:  $pH_{ind}$  Testwork Results

Test	Fe(T) (g/L)	Fe(3+) (g/L)	Fe(2+) (g/L)	As(5+) (g/L)	Cu(T) (g/L)	$pH_{ind}$
P1	1.50	1.50	0.00	1.03	29.0	1.61
P2	1.50	1.50	0.00	0.95	29.0	1.66
P3	1.60	1.60	0.00	0.98	18.0	1.50
P4	1.60	1.60	0.00	1.04	18.0	1.56
P5	2.30	2.30	0.00	1.05	18.0	1.59
P6	2.30	2.30	0.00	1.10	28.5	1.58
P7	2.30	2.30	0.00	1.10	28.5	1.60
P8	4.70	4.70	0.00	1.89	18.5	1.57
P9	7.42	7.42	0.00	1.59	6.10	1.67
P10	7.11	3.28	3.83	0.50	13.0	1.60
P11	9.39	2.59	6.80	0.50	13.0	2.00

The results of the  $pH_{ind}$  testwork show that each solution composition would require a specific pH set-point in order to produce a crystalline precipitate. The  $pH_{ind}$  testwork indicate the following trends:

- The  $pH_{ind}$  increases slightly with increasing copper and ferric Iron concentration
- The  $pH_{ind}$  increases dramatically with increasing ferrous Iron concentration
- The neutralisation pH set-point of PLS solution, containing ferrous Iron, would be higher than the neutralisation pH set-point of bioleach decant thickener overflow solution
- The neutralisation pH set-point of raffinate solution would be lower than the neutralisation pH set-point of PLS solution

add all  
Fe<sup>2+</sup> → Fe<sup>3+</sup>

The tests were all conducted at 90°C. It is expected that temperature would also affect the pH<sub>ind</sub> of the test solution. The pH<sub>ind</sub> testwork conducted on PLS solution, produced by the pilot plant in Chile, was not successful due to precipitate formation on heating of the solution. Further pH<sub>ind</sub> testwork will be conducted on bioleach decant thickener overflow solution produced by the pilot plant in Chile. Since the feed flow rate and composition to the neutralisation process is not expected to be constant for any length of time, the prospect of extremely accurate pH control and hence crystalline scorodite precipitation does not appear favourable.

## 6. BENCH SCALE NEUTRALISATION TESTS

Laboratory scale batch neutralisation experiments were conducted using synthetic solutions and PLS and bioleach decant thickener overflow solution produced by the pilot plant in Chile. The tests were conducted to:

1. Determine the extent of copper, iron and arsenic removal at pH values ranging from 1.0 to 3.0
2. Determine the extent of copper, iron and arsenic removal at temperatures ranging from 35°C to 85°C
3. Determine the suitability of various neutralising reagents to be used in the neutralisation process

The bench scale neutralisation tests give an indication of the pH set-point required to operate the continuous pilot plant. Bench scale neutralisation testwork was conducted, as the pH<sub>ind</sub> testwork was only successful on solutions that do not form an amorphous precipitate on heating. The pH set-point is dependent on the neutralisation solution and operating temperature. The tests indicate that neutralisation with amorphous precipitation is possible without major copper losses. Batch scorodite seeds testwork is still to be conducted on bioleach decant thickener solution produced by the pilot plant in Chile.

A summary of the batch neutralisation test conditions and feed compositions is shown in Table 3.

Table 3: Batch Neutralisation Test Conditions and Feed Compositions

Test	Temperature (°C)	pH reagent	Fe(T) (g/L)	Fe(3+) (g/L)	Fe(2+) (g/L)	As(5+) (g/L)	Cu(T) (g/L)
B1	85	CaO	4.06	4.06	0.00	1.82	25.2
B2	35	CaO	4.28	4.28	0.00	1.92	26.2
B3	85	MgO	8.06	2.70	5.36	0.40	11.7
B4	85	CaO	8.21	2.70	5.51	0.40	11.7
B5	85	CaO	7.90	7.23	0.00	1.60	5.95
B6	85	CaO	15.6	7.59	8.01	0.79	26.8
B7	60	CaO	15.6	7.59	8.01	0.79	26.8
B8	85	CaCO <sub>3</sub>	17.8	17.3	0.50	3.20	20.2
B9	60	CaCO <sub>3</sub>	17.8	17.3	0.50	3.20	20.2

### 6.1 Experimental Procedure

The batch neutralisation tests were conducted in agitated 2.5 dm<sup>3</sup> beakers placed on hot plates. The hot plates automatically maintained the solution at the required temperature. Analytical magnesium oxide, lime or limestone was added in a stepwise manner via a graduated pipette. Sample aliquots were removed at various pH values, immediately filtered and the filtrate submitted for chemical assay. The copper, arsenic and iron losses were based on chemical assay of the solution only. Washing of the precipitate was not conducted. The precipitate was not submitted for chemical assay due to the lack of sample produced. The copper, arsenic and iron losses and reagent consumptions per litre of bioleach solution were adjusted for the sample aliquot removal.

## 6.2 Results and Discussion

Detailed monitoring results of the batch neutralisation tests are shown in tables presented in Appendix 1. Graphical batch neutralisation profiles are shown in Figure 1 to Figure 9. Figure 1 and Figure 2 shows the copper, iron and arsenic removals for the neutralisation of synthetic bioleach decant thickener overflow solution, at 85°C and 35°C, using lime as the neutralising reagent.

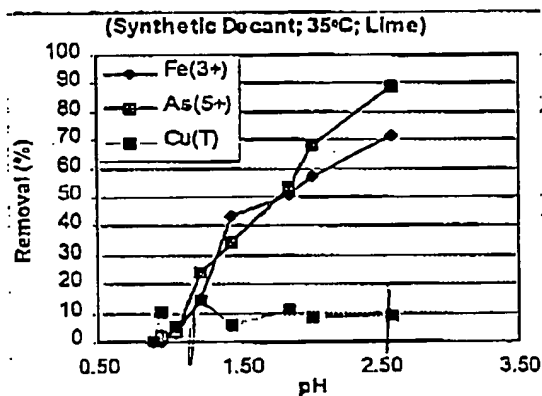


Figure 1: Batch Neutralisation Test B1

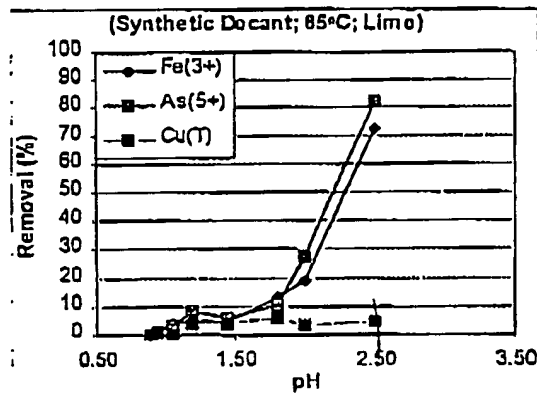


Figure 2: Batch Neutralisation Test B2

Figure 1 and Figure 2 show that higher pH levels are required for the 85°C test to achieve the same iron and arsenic removal as the 35°C test. The copper loss is lower in the 85°C test than in the 35°C test at corresponding pH levels. The initial pH of the synthetic bioleach decant thickener overflow solution is 0.89. Figure 3 and Figure 4 indicate the copper, iron and arsenic removals for the neutralisation of synthetic PLS solution using magnesium oxide and lime as the neutralising reagents. The tests were both conducted at 85°C.

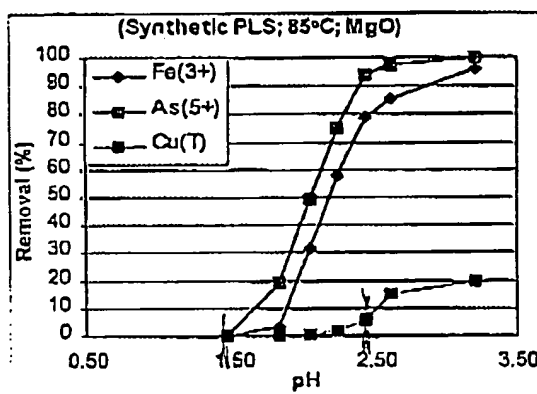


Figure 3: Batch Neutralisation Test B3

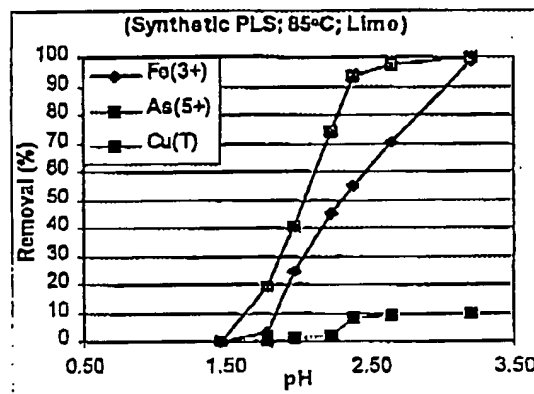


Figure 4: Batch Neutralisation Test B4

Magnesium oxide and lime appear to produce similar results in terms of iron and arsenic removal. The copper loss appears lower when using lime as the neutralising reagent. The difference can only be attributed to analytical error. Due to the reduced cost of lime versus magnesium oxide and the similarity of the results, magnesium oxide was not used in any further tests. The initial pH of the synthetic PLS solution is 1.47. The initial pH is higher than the initial pH of the synthetic bioleach decant thickener overflow solution due to the ferrous iron present in the solution. The continuous pilot plant neutralisation test C2 was conducted using the same test solution as batch tests B3 and B4.

Figure 5 shows the copper, iron and arsenic removals for the neutralisation of synthetic bioleach decant thickener overflow solution, at 85°C, using lime as the neutralising reagent.

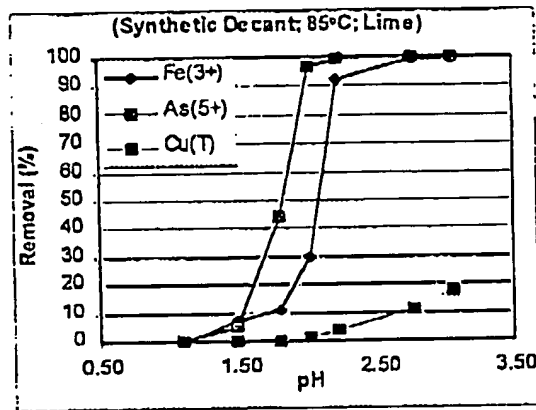


Figure 5: Batch Neutralisation Test B5

The continuous pilot plant neutralisation test C3 was conducted using the same test solution as batch test B5. As indicated by Figure 5, the pH set-point for the continuous neutralisation of bioleach decant thickener overflow solution is lower than continuous neutralisation of PLS solution. The batch neutralisation of synthetic solutions indicates that high arsenic removal (> 90%), is possible whilst not exceeding copper losses of 10%.

Figure 6 and Figure 7 show the copper, iron and arsenic removals for the neutralisation of PLS solution produced by the pilot plant in Chile using lime as the neutralising reagent. The tests were conducted at 85°C and 60°C respectively.

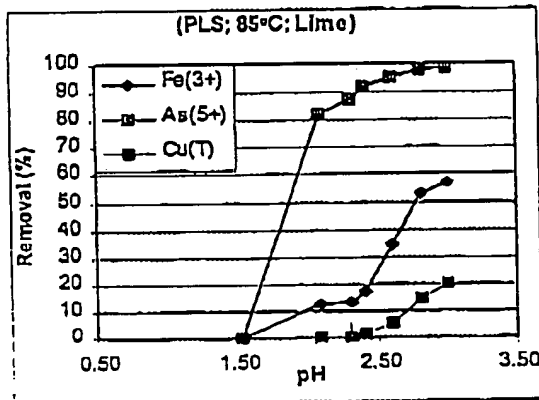


Figure 6: Batch Neutralisation Test B6

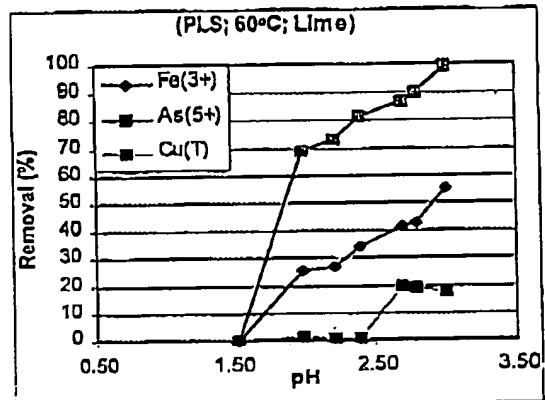


Figure 7: Batch Neutralisation Test B7

The PLS solution received contained an amorphous precipitate. The solution was filtered and the filtrate used in the batch and continuous neutralisation tests. The filter cake was submitted for chemical assay. The composition of the PLS filter cake is shown in Table 4.

Table 4: PLS Filter Cake Composition

Component	Content
Al	0.44 %
As	17.5 %
Cu	5.02 %
Fe	14.5 %
K	0.30 %
Mg	< 6.10 ppm
Mn	17.0 ppm

The precipitate contained in the PLS solution is reported to be formed after the ferric pre-leach thickener overflow solution has been collected and allowed to cool to ambient temperature over a number of days<sup>(4)</sup>. The stability of the precipitate was not tested.

When the PLS solution was heated, further amorphous precipitate was formed. The initial pH increase and the 80% and 70% arsenic removal, indicated in Figure 6 and Figure 7 respectively, is a result of the precipitate formed on heating of the solution. The batch neutralisation tests at a higher operating temperature resulted in increase arsenic removal at corresponding copper losses. The continuous pilot plant neutralisation tests C4 and C5 were conducted using the same solutions as batch neutralisation tests B6 and B7.

Figure 8 and Figure 9 indicate the copper, iron and arsenic removals for the batch neutralisation of bioleach decant thickener overflow solution produced by the pilot plant in Chile. The tests were conducted at 85°C and 60°C respectively. Limestone was tested as a neutralisation reagent due to the reduced reagent cost of limestone versus lime and magnesium oxide.

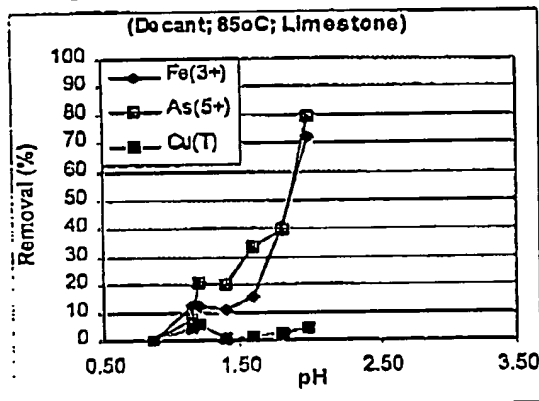


Figure 8: Batch Neutralisation Test B8

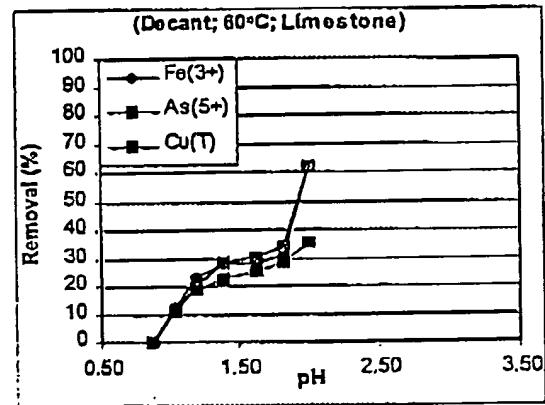


Figure 9: Batch Neutralisation Test B9

No precipitate was formed when the bioleach decant thickener overflow solution was heated. The copper loss is substantially lower at 85°C than at 60°C at corresponding pH levels. The continuous pilot plant neutralisation tests C6 to C8 were conducted using the same solutions as batch neutralisation tests B8 and B9.

The batch neutralisation tests indicate the following trends:

- The synthetic and pilot plant bioleach decant thickener overflow solutions have an initial pH of  $> 0.8$  whilst the synthetic and pilot plant PLS solutions have an initial natural pH of  $> 1.4$ . This is due to the ferrous iron present in the PLS solutions
- Heating of the PLS solution produced by the pilot plant in Chile, results in the pH increasing to  $> 1.9$ . Amorphous precipitation occurs on heating of the PLS, hence the use of scorodite seeds is no longer feasible for this PLS solution
- Copper losses, based on solution analysis, occurred in all the batch neutralisation tests conducted. The extent of copper loss is related to the arsenic removal, hence the aim of the continuous neutralisation tests should be to remove a portion of the arsenic present in the process stream whilst minimising the copper loss.
- The batch neutralisation tests at a higher operating temperature resulted in increased arsenic removal at corresponding copper losses
- Limestone is a suitable neutralisation reagent in terms of reagent cost and the range of pH control required. The limestone reagent consumption however, is approximately double the lime reagent consumption for the same pH adjustment

The batch neutralisation tests were used as an indication of the pH ranges to be used in the continuous tests, i.e.  $> 2.0$  for PLS solutions and  $< 2.0$  for bioleach decant thickener solutions.

## 7. NEUTRALISATION POSITIONS WITHIN THE BIOCOP® PROCESS

A number of options exist regarding the position of the neutralisation step within the BioCOP® process. The alternative process stream neutralisation options are as follows:

- ✓ 1. PLS solution produced by the ferric pre-leach
2. Bioleach decant thickener overflow solution
- ③ 3. Raffinate solution produced by the SX / EW circuit
4. Bioleach CCD wash water

Each neutralisation step position within the BioCOP® process has advantages and disadvantages.

### 7.1 PLS Feed Solution

The PLS feed solution, comprising the ferric pre-leach thickener and the bioleach CCD overflow solutions, contains both ferrous and ferric iron due to the reduction of ferric iron in the ferric pre-leach. The arsenic in the PLS solution is considered due to the recirculation of bioleach decant thickener and the bioleach CCD overflow solutions and not the dissolution of enargite in the ferric pre-leach. The advantages and disadvantages of neutralising the PLS solution are as follows:

#### Advantages

- Reduction of the ferric iron content of the PLS prior to SX thereby reducing the extraction of iron into the organic phase and degradation of the organic phase
- Reduction of the acid content of the PLS prior to SX
- Removal of precipitates present in the ferric pre-leach solution prior to SX hence reducing crud formation in the SX

#### Disadvantages

- High copper concentrations in the PLS may result in high copper losses
- If the ferric iron content of the PLS is too low, the arsenic removal may be limited
- Excessive heating of the PLS solution prior to SX if the neutralisation is conducted at  $85^{\circ}\text{C}$
- Largest solution flowrate of the neutralisation options

The BioCOP<sup>®</sup> process flowsheet showing the PLS solution neutralisation is shown in Figure 10.

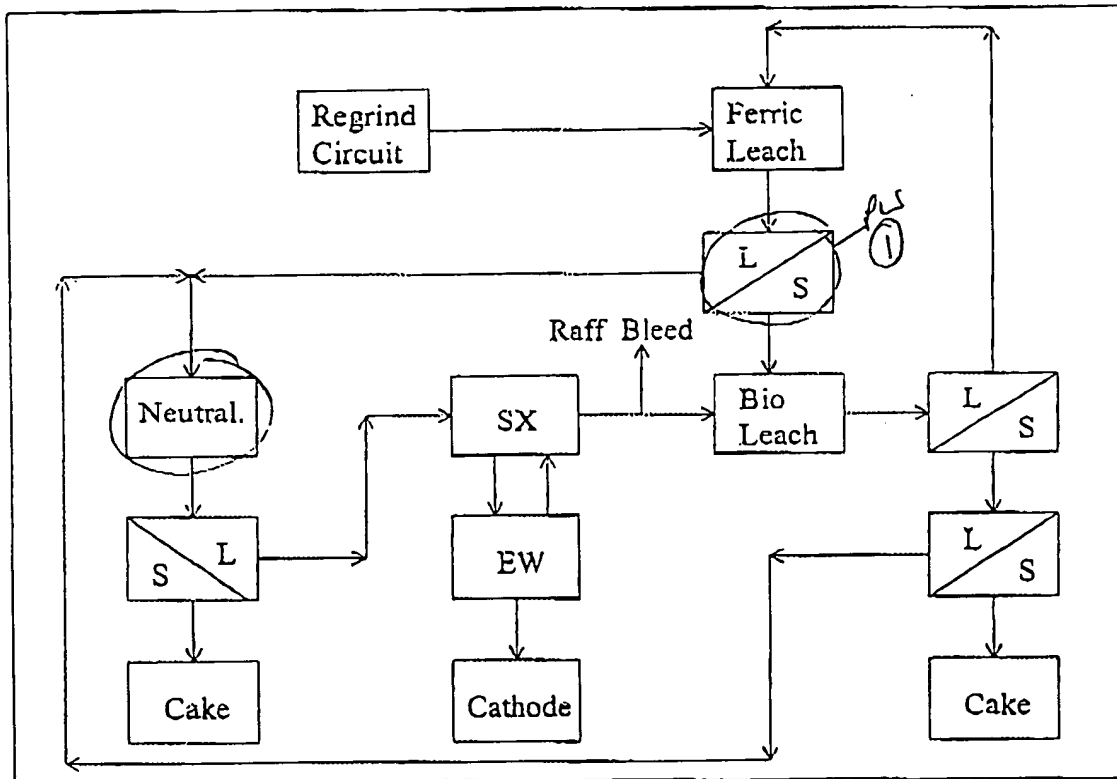


Figure 10: BioCOP<sup>®</sup> Process Flowsheet with PLS Neutralisation

## 7.2 Bioleach Decant Thickener Overflow Solution

The bioleach decant thickener overflow solution contains ferric iron and low levels of ferrous iron. The arsenic in the bioleach decant thickener overflow solution is due to the dissolution of enargite in the bioleach. The advantages and disadvantages of neutralising the bioleach decant thickener overflow solution are as follows:

### Advantages

- High ferric iron content of the solution to promote arsenic removal
- Heating of the solution prior to the ferric pre-leach
- Lower solution flowrate and copper content than the PLS solution

### Disadvantages

- Relatively high copper concentrations may result in high copper losses
- Reduction of the ferric iron content of the solution prior to the ferric pre-leach
- Reduction of the acid content of the solution prior to the ferric pre-leach
- The raffinate bleed will contain the arsenic that has been washed from the bioleach CCD thickener underflow solids

The BioCOP<sup>®</sup> process flowsheet showing the bioleach decant thickener overflow solution neutralisation is shown in Figure 11.

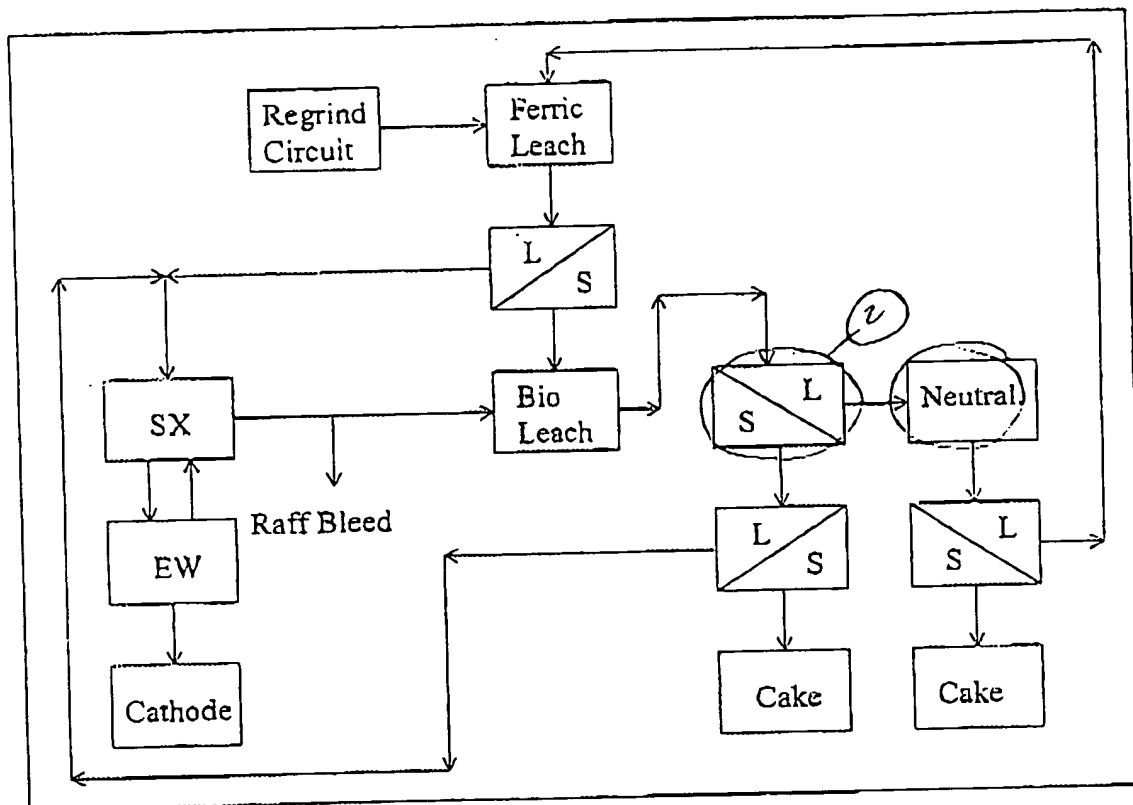


Figure 11: BioCOP<sup>®</sup> Process Flowsheet with Bioleach Decant Thickener Overflow Neutralisation

### 7.3 Raffinate Bleed Solution Produced by the SX / EW Circuit

The raffinate bleed solution produced by the SX / EX circuit contains both ferrous and ferric iron due to the reduction of ferric iron in the ferric pre-leach. The arsenic in the raffinate solution is considered due to the recirculation of bleached decant thickener overflow solution to the ferric pre-leach and not the dissolution of enargite in the ferric pre-leach. The advantages and disadvantages of neutralising the raffinate solution are as follows:

### Advantages

- Low copper concentrations should result in lower copper losses
- Lowest solution flowrate and copper content of the neutralisation options
- The neutralised raffinate bleed will only contain the arsenic that has not been removed from the raffinate bleed solution

### Disadvantages

- High acid content would result in large limestone consumption
- Low ferric iron content may limit the arsenic removal
- Reduced acid content of the neutralised raffinate bleed solution will decrease the usefulness of the raffinate bleed as a potential heap leach solution

The BioCOP<sup>®</sup> process flowsheet showing the raffinate solution neutralisation is shown in Figure 12.



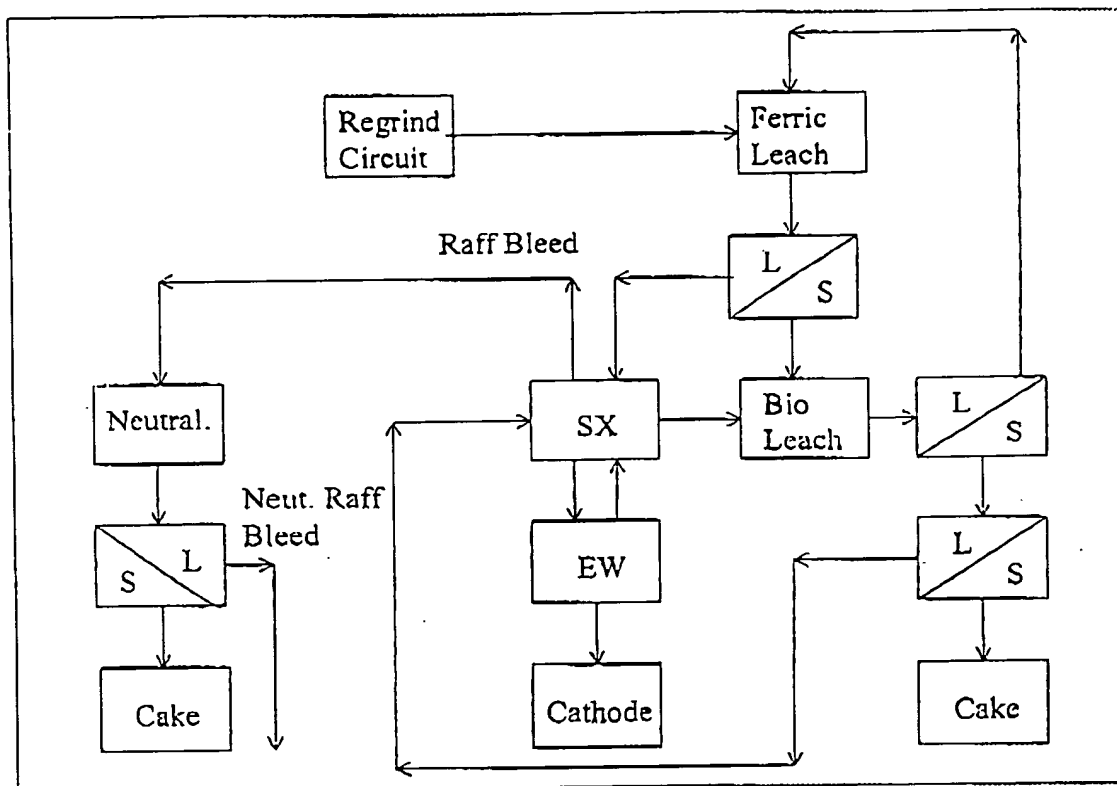


Figure 12: BioCOP® Process Flowsheet with Raffinate Neutralisation

#### 7.4 Bioleach CCD Wash Water

The bioleach CCD wash water solution obtained from washing the bioleach residue contains ferric iron and low levels of ferrous iron. The arsenic in the CCD wash water solution is due to the dissolution of enargite in the bioleach. The advantages and disadvantages of neutralising the bioleach CCD wash water solution are as follows:

##### Advantages

- High ferric iron content of the solution to promote arsenic removal
- Reduction of ferric iron content prior to SX
- Low solution flowrate and lower copper content than the PLS solution
- Low reagent consumption

##### Disadvantages

- Relatively high copper concentrations may result in high copper losses
- The raffinate bleed will contain the arsenic from the bioleach decant thickener overflow solution

The BioCOP® process flowsheet showing the bioleach CCD wash water neutralisation is shown in Figure 13.

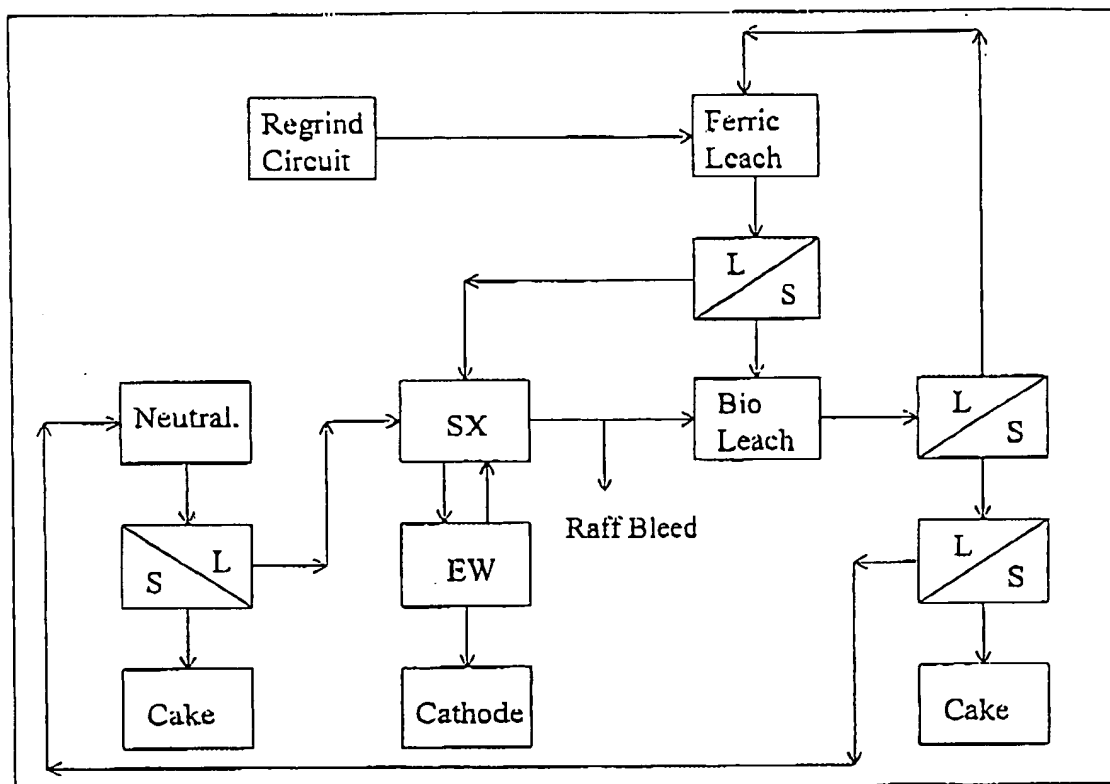


Figure 13: BioCOP® Process Flowsheet with CCD Wash Water Neutralisation

#### 7.5 Conclusions

Each neutralisation step position within the BioCOP® process flowsheet has advantages and disadvantages. Ideally the neutralisation step should be positioned to treat the PLS stream prior to SX to lower the ferric concentration entering the SX plant. Neutralisation of the PLS stream, however, may result in significant copper losses due to the high copper tenor of the solution. The neutralisation of raffinate bleed solution is the best option in terms of reduction of copper loss but has the major disadvantage of high limestone consumption. Neutralisation may also be performed on the bioleach decant thickener overflow solution and the CCD wash water solution. At these stages in the process, copper co-precipitation should be less significant due to the lower copper content of the respective streams. However, treating the bioleach decant thickener overflow solution will result in arsenic reporting to the raffinate stream due to not neutralising the arsenic in the CCD wash water solution and visa versa.

#### 8. PILOT PLANT NEUTRALISATION TESTS

A neutralisation pilot plant was commissioned in order to conduct a series of continuous neutralisation tests based on the criteria established during the batch neutralisation testwork. The objectives of the continuous neutralisation pilot plant tests were to:

1. Determine the efficiency of iron and arsenic removal from solution, and to determine the stability of the resultant product precipitates formed
2. To establish the extent of copper co-precipitation at the alternate neutralisation positions within the BioCOP® process
3. Determine the reagent consumption required to neutralise the BioCOP® process streams.
4. Provide neutralised solution samples for thickening and filtration testwork

The continuous neutralisation pilot plant tests were carried out on both synthetic and pilot plant PLS and bioleach decant thickener overflow solutions. Synthetic feed solutions were used initially whilst bulk samples were being generated by the Smarties pilot plant in Chile. The synthetic feed solutions were made up using copper sulphate, ferric sulphate, ferrous sulphate, sulphuric acid and arsenic pentoxide.

Continuous pilot plant tests were not conducted on bioleach CCD wash water as the stream composition is considered similar to that of bioleach decant thickener overflow solution. The raffinate solution produced by the SX / EW circuit was not neutralised in the pilot plant. The copper tenor is a great deal lower than the PLS tenor and hence the testwork on the PLS solution would give a worst case scenario of copper loss.

A summary of the feed characteristics of the solutions used in the continuous neutralisation testwork is shown in Table 5.

Table 5: Continuous Pilot Plant Neutralisation Feed Analysis

Test	Fe(T) (g/L)	Fe(3+) (g/L)	Fe(2+) (g/L)	As(5+) (g/L)	Cu(T) (g/L)
C1	6.51	6.51	0.00	1.01	13.9
C2	9.11	2.69	6.42	0.45	11.7
C3	7.90	7.90	0.00	1.72	5.99
C4	15.7	6.40	9.30	0.78	27.6
C5	16.0	6.40	9.60	0.79	27.6
C6	21.9	21.1	0.80	3.05	20.3
C7	21.9	21.1	0.80	3.05	20.3
C8	21.9	21.1	0.80	3.05	20.3

Continuous tests (C1 – C3) were conducted on synthetic solutions. Continuous tests (C4 – C8) were conducted on PLS and bioleach decant thickener overflow solution generated by the Smarties pilot plant in Chile.

#### 8.1 Pilot Plant Description and Experimental Procedure

For all the continuous neutralisation tests, the plant was configured as 4 reactors in series, each having an aerated live volume of 6.5 litres. The reactors were each agitated with pitch blade impellers at approximately 275 rpm. Air was sparged into each reactor in order to convert ferrous iron to ferric iron and to aid with mixing. The basic flowsheets of the continuous neutralisation pilot plant tests are shown in Figure 14 and Figure 15.

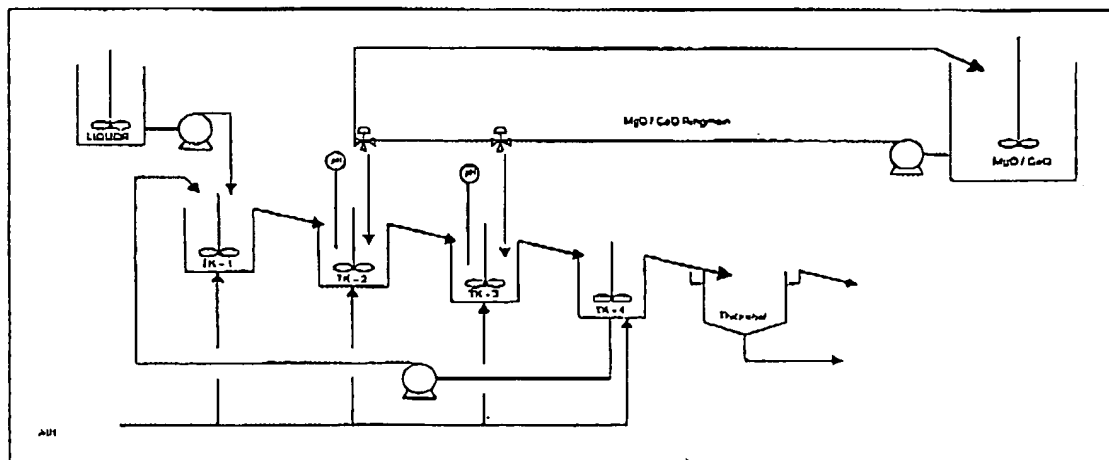


Figure 14: Basic Flowsheet of the Continuous Neutralisation Circuit: Tests (C1 – C5)

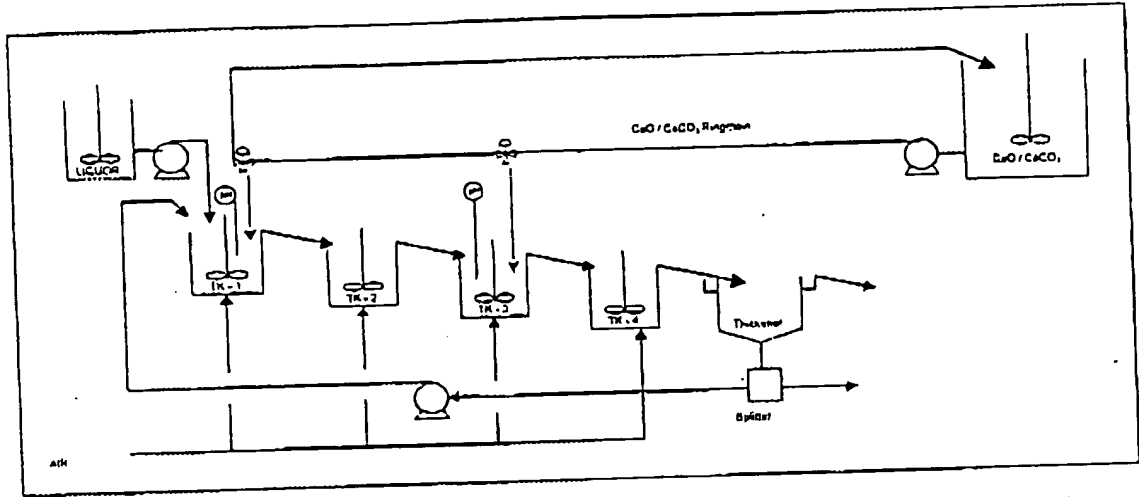


Figure 15: Basic Flowsheet of the Continuous Neutralisation Circuit: Tests (C6 – C8)

Magnesium oxide, lime, or limestone was agitated in a make-up vessel, and circulated via a ring main using a peristaltic pump. Magnesium oxide was used as the neutralising reagent for tests (C1 – C2). Lime was used for tests (C3 – C5) and limestone was used for tests (C6 – C8). The magnesium oxide concentration was initially made up to 100 g/L but for subsequent tests, lime and limestone was made-up to 20 g/L to promote stable and constant reagent addition. The pH was measured and controlled in reactor 1, reactor 2 and reactor 3 by magnesium oxide, lime or limestone addition from the ring main via solenoid valves.

The continuous neutralisation tests were initially performed with no recycle (C1). For tests (C2 – C5), slurry from the forth reactor was recycled via a peristaltic pump back into the first reactor. For tests (C6 – C8), thickener underflow was recycled via a peristaltic pump back into the first reactor. The recycle ratio varied from 3: 1 to 1:1 (feed mass flow : recycle mass flow). The recycle was introduced to improve precipitation by providing seeds to promote growth of larger particles. Feed liquor was pumped to the first tank from a feed reservoir via a dosing pump at the required feed rate. Dilution water was added to the last three reactors to compensate for solution loss due to evaporation.

Continuous tests (C1 – C2) were operated at 75°C and 80°C respectively, whilst heating elements were being manufactured. A water geyser heating system initially heated the pilot plant reactors. For Phase 1 of the continuous tests (C4 – C5), no pH control was used to establish the effect of heating the slurry to 85°C and 60°C during continuous operation. Continuous tests (C5 – C6) were operated at 60°C to establish whether continuous neutralisation could be conducted at a lower temperature whilst still achieving the same results as the continuous test conducted at 85°C (C3 – C4 and C7). Continuous test C8 was conducted to produce neutralised slurry for settling and filtration testwork.

A summary of the operating conditions used during each of the continuous neutralisation tests is given in Table 6.

Table 6: Continuous Pilot Plant Neutralisation Test Conditions

Test Number	C1	C2	C3	C3	C3	C4	C4
Phase	1	1	1	2	3	1	2
pH Control Reactors	1 & 3	2 & 3	2 & 3	2 & 3	2 & 3	-	2 & 3
pH Setpoints	1.50 & (1.80)	2.00 & 2.20	1.75 & 1.80	1.80 & 1.90	1.90 & 2.00	-	2.15 & 2.25
Feed : Recycle Ratio	-	3:1	2:1	2:1	2:1	2:1	2:1
Operating Temperature	75°C	(80°C)	(85°C)	(85°C)	(85°C)	(85°C)	(85°C)
Plant Retention (hrs)	8.6	8.6	13	13	13	26	26
Neutralising reagent	MgO	MgO	CaO	CaO	CaO	-	CaO
Reagent Consumption (g/L)	8.25	11.7	2.50	3.22	3.75	-	3.45
Test Number		C5	C5	(C6)	(C6)	(C7)	(C8)
Phase		1	2	1	2	2	1
pH Control Reactors		-	2 & 3	1 & 3	1 & 3	1 & 3	1 & 3
pH Setpoints		-	2.15 & 2.25	1.60 & 1.85	1.60 & 1.75	1.60 & 1.75	1.60 & 1.75
Feed : Recycle Ratio		1:1	1:1	1:1	1:1	1:1	1:1
Operating Temperature		60°C	(60°C)	60°C	60°C	85°C	60°C
Plant Retention (hrs)		26	26	26	26	26	26
Neutralising reagent		-	CaO	CaCO <sub>3</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub>	CaCO <sub>3</sub>
Reagent Consumption (g/L)		-	1.81	4.05	3.73	3.91	3.71

During each continuous neutralisation test, the following parameters were monitored on an hourly basis to ensure that stable operation was achieved and maintained:

1. Level in the feed liquor reservoir
2. Level in the MgO / CaO / CaCO<sub>3</sub> make-up tank
3. pH in each reactor
4. Temperature in each reactor
5. Final reactor / thickener overflow volume

Once stable operation of the pilot plant was achieved, the product overflow from reactor 4 or the thickener was collected for a minimum test period of 8 hours and filtered. Selected filter cakes were submitted for TCLP (Toxicity Characteristic Leaching Procedure) testing. The corresponding solutions were submitted for chemical analyses. On completion of a continuous pilot test, the reactors were drained and the slurry from each of the reactors filtered and sent for analysis together with the filtrate. The filtrate was analysed for copper, iron and arsenic in solution and the filter cake submitted for XRD analysis. XRD analysis of the filter cake was conducted to indicate whether the precipitate formed was crystalline or amorphous in nature.

## 8.2 Results and Discussion

The copper, iron and arsenic removals and product precipitate stability attained for the various tests are reported in Table 7. The solution copper, iron and arsenic concentration profiles for the continuous neutralisation tests are shown in detail in Appendix 2.

22 0.3 1.6 1.7 1.9

Table 7: Summary of Continuous Pilot Plant Results

Test Number	C1	C2	C3	C3	C3	C4	C4
Phase	1	1	1	2	3	1	2
Residue solution analysis (g/L)							
Fe(T)	9.62	7.01	4.89	2.97	3.61	8.44	6.52
As(5+)	2.27	0.12	0.81	0.22	0.29	0.13	0.06
Cu(T)	25.6	10.1	4.67	(3.93)	(6.73)	20.4	20.1
Removal by solution analysis (%)							
Fe(T)	46.3	12.8	32.9	61.4	57.5	35.5	50.2
As(5+)	18.4	69.2	64.6	86.9	84.3	80.0	91.2
Cu(T)	0.50	2.17	(3.7)	(30.8)	(40.2)	13.0	12.6
Removal by solution and solid precipitate analysis (%) – precipitate not washed							
Fe(T)	-	11.0	-	-	37.0	-	17.5
As(5+)	-	82.7	-	-	91.3	-	54.9
Cu(T)	-	0.68	-	-	1.19	-	1.54
Removal by solution and solid precipitate analysis (%) – precipitate washed							
Fe(T)	-	-	-	-	39.1	-	-
As(5+)	-	-	-	-	76.8	-	-
Cu(T)	-	-	-	-	0.40	-	-
TCLP Extracts (ppm) – precipitate not washed							
Fe(T)	0.63	409	-	-	26	-	224
As(5+)	10	1.40	-	-	0.91	-	1.15
Cu(T)	0.91	819	-	-	235	-	1128
TCLP Extracts (ppm) – precipitate washed							
Fe(T)	-	-	-	-	3.32	-	-
As(5+)	-	-	-	-	0.19	-	-
Cu(T)	-	-	-	-	35.1	-	-
Test Number	C5	C5	C6	C6	C7	C8	
Phase	1	2	1	2	1	1	
Residue solution analysis (g/L)							
Fe(T)	14.1	12.4	18.8	19.3	13.6	23.6	
As(5+)	0.28	0.24	1.72	2.55	0.81	2.95	
Cu(T)	25	19.7	14.8	18.0	18.0	20.7	
Removal by solution analysis (%)							
Fe(T)	3.10	7.00	24.4	29.7	38.1	3.48	
As(5+)	61.0	63.5	43.6	33.1	73.4	13.0	
Cu(T)	12.3	14.4	(26.9)	(28.8)	(21.0)	8.0	
Removal by solution and solid precipitate analysis (%) – precipitate not washed							
Fe(T)	-	6.16	18.5	-	17.3	18.0	
As(5+)	-	60.2	28.3	-	45.6	4.34	
Cu(T)	-	0.43	2.00	-	0.84	2.23	
Removal by solution and solid precipitate analysis (%) – precipitate washed							
Fe(T)	-	-	-	20.0	32.0	12.2	
As(5+)	-	-	-	29.1	78.9	3.03	
Cu(T)	-	-	-	0.22	0.13	0.09	
TCLP Extracts (ppm) – precipitate not washed							
Fe(T)	-	227	75.0	-	26.0	553	
As(5+)	-	0.76	15.0	-	4.00	63	
Cu(T)	-	839	299	-	305	833	
TCLP Extracts (ppm) – precipitate washed							
Fe(T)	-	-	-	0.51	0.57	5.3	
As(5+)	-	-	-	0.45	0.33	0.70	
Cu(T)	-	-	-	0.29	1.10	0.45	

XRD analysis of the precipitate indicated that the crystalline material formed was either jarosite or gypsum. Crystalline scorodite was not detected in any of the continuous neutralisation tests. The detection limit for crystalline scorodite is 3%, hence, if there was crystalline scorodite produced then it was below the detection limit.

According to the solution analysis conducted on the residue solution, the copper removals are unacceptably high. The copper removals by solution and solids analysis on the precipitate show substantially lower copper losses. The difference in copper loss can be attributed to the method of solution sample collection. Each hour an overflow sample was collected, decanted and an aliquot of the decant submitted for chemical assay as the overflow sample. The remaining decant and solids was filtered through the previous hourly overflow filter cakes. This has the effect of washing the solids. This was confirmed by higher copper, arsenic and iron concentrations in the filtrate than in the decanted overflow samples. The minimum arsenic removal for the continuous tests was 33% by solution analysis and 29% by solution and solids analysis of the precipitate. The maximum copper loss for the continuous tests was 40% by solution analysis and 2% by solution and solids analysis of the precipitate.

For continuous tests (C4 – C5), a period of heating of the reactors, to the required operating temperatures, was carried out before neutralising reagent addition to establish the effect of heating the slurry to 85°C and 60°C during continuous operation. Heating of the reactors resulted in copper and arsenic removals of > 12% and 60% respectively. Further neutralising reagent addition increased the copper and arsenic removals.

For continuous tests C4 and (C6 - C8), precipitate product samples were washed at pH 1.2 and submitted for chemical assay and TCLP testing. The washing ratio was 1:1 (slurry volume : wash solution volume). Washing of the precipitate lowered the arsenic and copper removals and the extracts by TCLP tests.

Environmental legislation for disposable liquid waste stipulates that the arsenic and iron content in solution should not exceed 0.5 ppm and 1.0 ppm respectively. For all the continuous neutralisation tests, the effluent arsenic and iron content of the neutralised slurry filtrate contained levels exceeding environmental legislation limits. Since the neutralised slurry filtrate is returned to the BioCOP® process, the environmental legislation limits do not apply. The precipitate formed during the neutralisation process will be thoroughly washed and filtered before disposal and the solution produced also returned to the BioCOP® process. The washed precipitates in terms of arsenic extraction, show that the neutralisation products are stable. The allowable EPA maximum concentration for arsenic in extracts from solid wastes is 5 ppm.

The continuous neutralisation tests indicate the following trends:

- Crystalline scorodite was not detected in any of the continuous neutralisation tests. The precipitate formed was amorphous ferric arsenate with limited amounts of jarosite or gypsum.
- Heating alone of the PLS solution produced by the pilot plant in Chile, resulted in copper and arsenic removals
- Higher operating temperatures resulted in lower copper losses and higher arsenic removals
- Washing the precipitate at pH 1.2 resulted in lower arsenic and copper removals and lower extracts by TCLP tests
- Provided washing of the amorphous precipitate is undertaken, the neutralisation products are stable
- Limestone is a suitable neutralisation reagent in terms of reagent cost and the range of pH control required. The limestone reagent consumption however, is approximately double the lime reagent consumption for the same pH adjustment

## 9. LIQUID-SOLID SEPARATION TESTS

Continuous test C8 was conducted to produce neutralised product samples for thickening and filtration testwork. Alister Mac Donald of Mac One undertook the thickening and filtration testwork. The basis of calculations used were:

Solids S.G.	2.500 Estimated
Liquid S.G.	1.115 by hydrometer
Slurry R.D.	1.123 by hydrometer

### 9.1 Polymer Selection

Small aliquots of slurry were arranged on a spot test sheet and mixed with low dosages of 25 flocculant polymers. The spot test results, in terms of flocculation, were subjectively rated from "excellent" to "none." Magnafloc E10, 352, 368, E24, 919, and Zetag 41 were found to be the most suitable flocculants tested. Settling tests on 80 millilitre neutralised product samples were conducted using only the suitable polymers as indicated by the spot tests.

Single-stage flocculant addition required much larger flocculant dosages than two-stage flocculant addition. The best result was obtained when the first flocculant addition was given vigorous mixing and the second flocculant addition given a short mix. A two-stage addition of the relatively cheaper Magnafloc E10 showed the strongest floccule formation compared to the other more expensive flocculants. A minimum total dosage of 2.5 ppm was required for effective flocculation. Dull green supernatant solutions were produced during the settling tests. Sparkling clear or blue supernatants were not achieved.

### 9.2 Bulk Sedimentation Tests

Bulk sedimentation tests using 250 millilitre neutralised product samples were conducted at various stirrer speeds and flocculant dosages. The best flocculant combinations were then tested at low dosages. To achieve optimum results at a stirrer speed of 300 rpm, 30 seconds of stirring is required for the first flocculant dosage whilst 3 to 5 seconds of stirring is required after the second flocculant dosage. The most durable floccules were produced by the combination of various flocculants and Magnafloc E10. The supernatants produced during the bulk sedimentation tests were never sparkling clear but a dull hazy green. Any significant dilution of the supernatants resulted in a colour change of the supernatants to dark brown.

A two-stage or multiple flocculator system is thus recommended for the effective flocculation of the neutralised product. Magnafloc E10 dosed at approximately 0.4 ppm at two dosing points is likely to be the optimum method of flocculant addition. At this recommended dosage, there is almost no danger of flocculant carry-over in the supernatant solutions.

### 9.3 Neutralised Product Thickening Test

The remainder of the neutralised product sample supplied for the liquid-solid separation testwork was thickened using approximately 0.4 ppm Magnafloc E10 dosed at two dosing points. The sediment produced by thickening and used in the filtration tests was approximately 55% solids. It was observed that the sediment was a mixture of gritty pale crystals and fine ferric slimes. A flocculant dosage of 55 g/t could not induce fluidity to the large proportion of grit, as there was not enough fine slime to lubricate or levitate the crystals.



The dense nature of the sediment produced could cause problems on the ultra-high capacity clarifiers since these clarifiers are not equipped with a strong rake. Even a steeply sloping settler base may not be adequate to ensure continuous underflow pumping without a rake. The underflow material looks suitable for depositing on a slimes dam if no further dewatering was required due to the solute content of the underflow material. There was some scum produced on the supernatant surface. The use of a high capacity thickener such as the Supaflo High Rate Thickener would give the clearest overflows and would prevent some of the scum formation. Scum boards will be required for at the overflow launder.

#### 9.4 Filtration Tests

Some supernate was added to the sediment produced in the thickening test to aid in flocculant distribution. Filter tests simulating pan or belt filtration were conducted on samples of between 70 and 90 millilitres. A needle felt cloth was used in a 0.002 m<sup>2</sup> laboratory filter. The cloth was covered with a disc of Whatman's no. 54 paper. The paper was renewed for each test. No consequent response to flocculation was noticed in the first six filtration tests conducted with the paper membrane. No air purging took place, even after ten minutes, with dosage as high as 300g/ton. The filter cakes appeared dry but there was no dramatic reduction in vacuum at any point. The last two filtration tests were conducted without the paper membrane. When the paper element was omitted, the filtration was complete in 8 seconds with a significant air purge during the drying period. A dirty filtrate was produced without clogging the cloth.

Filtration of the thickened neutralised product would be practical process for final dewatering provided the correct filter cloth is selected. The horizontal vacuum belt filtration area requirement would be approximately 0.20 m<sup>2</sup> per hourly ton of solids at a dosage of 200 g/t and 0.23 m<sup>2</sup> per hourly ton of solids at a dosage of 100 g/t. The final moisture would be approximately 30%. One ton of solids per hour would require a diaphragm / chamber press with a total chamber volume of 0.18 m<sup>3</sup>, e.g., a 14-chamber press of 470 x 470 x 60 mm per chamber with a ten minute cycle time. This type of press would produce cakes in the region of 15% moisture.

The filtration testwork conducted did not include filtration behaviour at low flocculant dosages. The appearance of the sediment appeared suitable for press filtration without flocculation provided the sediment is pumped with positive displacement pumps. The filtrate and cloth regeneration wash solutions can be recycled to the thickener via the flocculators.

#### 9.5 Recommendations

Magnafloc E10 should be dosed in two stages to the decanting thickener. The flocculant should be made up at 1g/L. The dosage should be as dilute as possible to a stirred vessel with a 30 second residence time followed by an inline stirrer situated in the feed-well from which the slurry should emerge gently into the feed-well. This can be achieved by designing the feed-well as a flocculator as used in some Supaflo feed-wells. Feed slurry should be de-aerated inside the feed well. The mixing time for the second flocculant dosage should be between 3 and 5 seconds. The dosage to aim for is 0.40 g/m<sup>3</sup> per dose. The first and second dosages should be split equally, i.e. 50/50, with provision for adjustment toward 30/70 or 70/30 splitting.

High capacity thickeners such as the Supaflo or Delkor thickeners should be better for clarity and reliability than an ultra-high capacity (E-Cat type) clarifier, due to the dense and cohesive nature of the sediment. The thickener rake should be given enough torque capacity for heavy sediment formation. The underflow pump should be a positive displacement pump to limit flocculant damage before filtration. The area required per hourly cubic metre of feed is 0.14 m<sup>2</sup>. This equates to 10.69 m<sup>2</sup> per hourly ton of solids. The underflow at 50% to 55% solids may block oversized pipelines, hence, the suction and delivery lines should be as short as possible. For suction and delivery line pipe sizing, the sediment should be treated as coarse sand from sand dumps. Provision should be made for a scum board to exclude scum from the overflow.

With proper flocculation, a horizontal filter belt will be ideal for the duty on the thickened material. The filtrate would contain significant slimes for return to the thickener. The area requirement would be about 0.25 m<sup>2</sup> per hourly ton of solids. The final moisture would be between 27% and 30%. This filter may require flocculation. The flocculant recommended is Magnafloc E10 at a dosage of between 60 and 100 g/ton solids. The flocculator should be in the filter feed area and the flocculant delivered onto a spreader in the filter feed pan. The flocculator should have a residence time of less than 5 seconds.

To achieve a final cake moisture of less than 30%, a diaphragm / chamber press should be used. The Larox, Baker Hughes or Water Engineering diaphragm / chamber presses are recommended. This would reduce the cake moisture to approximately 15% and produce cakes that would not stick on any conveyor in the disposal system. The system does not demand flocculation, but would perform better if the thickener underflow were not deflocculated by the choice of filter feed equipment.

## 10. CONCLUSIONS

The PLS solution produced by the pilot plant in Chile produced amorphous precipitate when heated, thus coating the scorodite crystals used for crystal seeding and crystalline growth. The bioleach decant thickener overflow solution does not form amorphous material when heated and hence scorodite seed testwork may be beneficial.

The batch neutralisation tests indicate that both the synthetic and pilot plant PLS and bioleach decant thickener overflow solutions have different initial natural pH's due to the ferrous iron present in the PLS solutions. Heating of the PLS solution produced by the pilot plant in Chile, results in an increase in pH and amorphous precipitation. The prevalence of amorphous precipitation and the tight plant operation required for crystalline scorodite crystallisation has shown that the Hatch / Hydro-Terra process is not suitable for BioCOP<sup>®</sup> product neutralisation. \*

Heating of the PLS solution produced by the pilot plant in Chile to the required operating temperatures of 85°C and 60°C, resulted in copper and arsenic removals. This indicates that heating during continuous neutralisation of BioCOP<sup>®</sup> product streams aids arsenic removal but the pH level should be such as to limit copper losses. Higher operating temperatures resulted in lower copper losses and higher arsenic removals.

The effluent arsenic and iron content of the neutralised slurry filtrate, produced during the continuous neutralisation tests, exceeded environmental legislation limits. The neutralised slurry filtrate will be returned to the BioCOP<sup>®</sup> process, hence the environmental legislation limits do not apply. Washing the precipitate product lowered the arsenic and copper removal and copper, arsenic and iron extracts by TCLP tests. The precipitate formed during the neutralisation process will be thoroughly washed and filtered before disposal and the solution produced also returned to the BioCOP<sup>®</sup> process. The washed precipitates formed during the continuous neutralisation tests, in terms of arsenic extraction, are stable and meet the allowable EPA limits.

Thickening is required before filtration. Underflows containing 50% solids are possible provided a strong raking mechanism is used. Horizontal belt vacuum filtration will produce cakes at 30% moisture on 0.25 m<sup>2</sup> area per hourly ton of solids. A diaphragm press would improve the cake moisture to 15%.

The neutralisation of raffinate solution is the best option in terms of reduction of copper loss but has the major disadvantage of high neutralisation reagent consumption. The raffinate solution produced by the SX / EW circuit was not neutralised in the pilot plant as the copper tenor is a great deal lower than the PLS tenor and hence the testwork on the PLS solution would give a worst case scenario of copper loss.

11. RECOMMENDATIONS

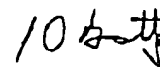
The pilot neutralisation plant should be operated in parallel to the pilot plant or demonstration plant in Chile. This will allow for the process optimisation and determination of the recycling effect of returning neutralised solution to the BioCOP® process.

12. REFERENCES

1. Cock, C. (1998) "BioCOP® Product Neutralisation: Progress Report", BILLITON Process Research Confidential Report No 98/137.
2. Droppert, D.J. (1998) "Laboratory Study on Arsenic and Iron Precipitation BioCOP® Solutions", Joint Project with Hatch Africa for Billiton S.A. April 1998.
3. Droppert, D.J. (1996) "The Ambient Pressure Precipitation of Crystalline Scorodite from Sulphate Solutions", MSc Dissertation, McGill University, Montreal Canada
4. Rorke, G.V. (1999) BILLITON Process Research, Private Communication – June 1999.



P I Harvey  
PRINCIPAL RESEARCH METALLURGIST



J D Batty  
PROCESS MANAGER